

Three-dimensional microfabrication by two-photon-initiated polymerization with a low-cost microlaser

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Fabrication of submicrometer structures by two-photon-initiated polymerization is performed with an inexpensive and low-power microlaser. This is made possible by the design of photoinitiators with strong two-photon absorption cross sections. We analyze the influence of both material properties and irradiation conditions on the two-photon polymerization rate and show that resins based on our highly sensitive two-photon photoinitiator can be solidified with microlaser excitation, whereas commercial UV photoresins require ultrashort and intense laser pulses. © 2002 Optical Society of America

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Photopolymerization initiated by two-photon absorptivity (TPA) is an interesting method for the fabrication of complex micrometer-size three-dimensional (3D) structures.¹⁻⁹ When a chromophore acting as a photoinitiator is excited by the simultaneous absorption of two photons, it can chemically activate polymerization reactions, leading to the formation of solid structures. Since the absorption rate depends on the square of the incident laser intensity, TPA polymerization benefits from a large penetration depth and tight confinement of the excitation volume about the focal point. Thus, TPA polymerization provides a very simple and straightforward way to produce intricate 3D structures with high resolution. The wide range of microstructures of arbitrary complexity that can be produced by this technique should find applications in microfluidics, microelectromechanical systems, 3D integrated optical components, and biomedical microdevices (e.g., for drug delivery, manipulation of biological objects).

Recently, two-photon-induced polymerization was used to produce integrated optical devices,³ optical memories,⁴ photonic bandgaps,⁴⁻⁶ and micromachines.^{7,8} However, an important limitation to the widespread application of this attractive approach arises from the weak sensitivity of commercial UV photopolymers to TPA excitation: They require high laser intensities and substantial exposure times. The necessity to employ lasers with ultrashort pulses, high peak powers, and large repetition rates is not only onerous but also may damage the material, so that, in practice, only a small intensity window can be used for safe fabrication. In this context it seems interesting to identify molecules that display good initiation efficiency together with a strong TPA. Such an approach would make it possible to reduce both the laser intensity and the exposure time. Up to now, only a few studies in this direction have been undertaken.^{4,9-11}

We recently reported the design and synthesis of new chromophores that exhibit high TPA in the

visible spectral range (450–550 nm) and are able to photochemically initiate the polymerization of acrylate monomers.¹¹ These new chromophores are based on a *D*– Π –*D* structure (where *D* is an amino donor and Π is a weak conjugated bridge, biphenyl or fluorene).^{4,12} Our results show that resins based on these photoinitiators are orders of magnitude more sensitive to TPA excitation than are conventional UV photoresins.

In this Letter we demonstrate the possibility of using low-power microlaser TPA-initiated polymerization. First, a simple model is proposed to relate the progression of the photopolymerization reaction to material and laser irradiation characteristics. On the basis of this model, we can compare our material with commercial UV systems, showing that lasers with moderate intensities and low repetition rates are able to induce TPA polymerization of resins based on our photoinitiator. An example of 3D microstructure fabricated with a low-cost microlaser is given.

For our experimental conditions, we consider the basic chemical processes involved in two-photon polymerization to be those shown Fig. 1. Under laser irradiation, the photoinitiator dye can be excited by simultaneous absorption of two photons. Then, it undergoes an energy-transfer reaction with an acrylate monomer, resulting in the creation of radicals that are able to initiate the chain polymerization reactions. The growth of chain radicals is restrained by termination reactions. Below, we assume that bimolecular

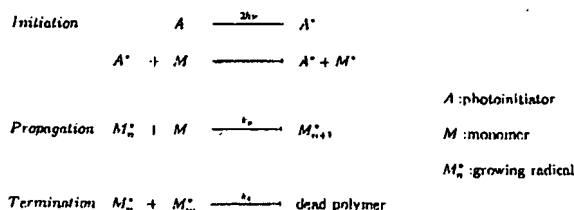


Fig. 1. Basic steps of polymerization.

recombination between propagating radicals is the predominant termination process.^{13,14}

The polymer structure that is fabricated has to resist the developing stage when unexposed resin is washed away. It should also possess adequate mechanical strength. Therefore, a sufficient degree of cross linking has to be achieved. The progression of the cross-linking reactions under two-photon excitation for given exposure conditions and material properties is derived below.

The degree of polymerization can be estimated through the quantity of monomer that is converted to polymer. The rate of monomer conversion can be considered equal to the rate of propagation and is given by Eq. (1), where k_p is the rate constant for propagation, $[M]$ is the monomer concentration, and $[M^*]$ is the total concentration in chain radicals:

$$-d[M]/dt = k_p[M^*][M]. \quad (1)$$

The evolution of the concentration in propagating radicals $[M^*]$ results from a competition between the initiation and termination rates, as shown in Eq. (2), in which R_i stands for the initiation rate and k_t is the rate constant for termination:

$$d[M^*]/dt = R_i - 2k_t[M^*]^2. \quad (2)$$

We consider Eqs. (1) and (2) to describe completely the kinetics of the polymerization process. In this model the influence of scavengers such as oxygen is overlooked. Diffusion and other nonlocal phenomena are not taken into account either.

Although pulsed lasers are used to generate the radical species, the initiation rate is assumed to be constant in time, since the cycle time of lasers is usually fast compared with the lifetime of growing radicals.¹³ Equation (3) gives an expression of the average initiation rate, which depends on the rate of production of excited photoinitiators by TPA and the efficiency of the energy-transfer process leading to the formation of radicals:

$$R_i = \Phi \frac{\sigma_{\text{TPA}}[A]}{2(\hbar\omega)^2} \left(\int_{\text{pulse}} I^2 dt \right) F. \quad (3)$$

In Eq. (3), Φ is the quantum yield for radical generation, i.e., the probability that an excited photoinitiator will give rise to a radical; σ_{TPA} is the TPA cross section of the initiator dye; $[A]$ is the concentration in the photoinitiator; $\hbar\omega$ is the photon energy; $(\int_{\text{pulse}} I^2 dt)$ is the square of the light intensity integrated over one pulse; and F is the repetition rate of the laser.

Solving Eqs. (1) and (2) yields the progression of the polymerization reaction: The evolution of the concentration of radicals is expressed in Eq. (4), and the density of monomer converted to polymer is given by Eq. (5). The laser is switched on at $t = 0$. During exposure, $[M^*]$ increases until it reaches its steady-state value, $[M^*]_s = [R_i/(2k_t)]^{1/2}$:

$$[M^*] = [M^*]_s \tanh(2k_t[M^*]_s t), \quad (4)$$

$$M_{\text{consumed}} = [M]_i \{1 - [\cosh(2k_t[M^*]_s t)]^{-k_p/2k_t}\}. \quad (5)$$

$[M]_i$ is the initial concentration of monomer.

A close approximation of Eq. (5) is given by $M_{\text{consumed}} = [M]_i[1 - \exp(-k_p[M^*]_s t)]$ when exposure

times are long compared with $1/k_t[M^*]_s$. For the range of exposure times that we use experimentally (~ 10 ms), the quantity $1/\tau = k_p[M^*]_s$ can be considered the rate of polymerization. The influence of laser and material parameters on this rate is detailed in Eq. (6), where $K_i = \Phi\sigma_{\text{TPA}}[A]$ and $K_t = (\int_{\text{pulse}} I^2 dt)F/[2(\hbar\omega)^2]$:

$$\frac{1}{\tau} = \frac{k_p}{\sqrt{2k_t}} K_i^{1/2} K_t^{1/2}. \quad (6)$$

In Eq. (6), there are contributions from the reactivity of the monomer and propagating radicals (k_p and k_t), the properties of the photoinitiator (K_i), and the characteristics of the laser source and exposure geometry, i.e., intensity, pulse duration, and repetition rate (K_t). Therefore, Eq. (6) can be used to compare the polymerization speed obtained with different resins and irradiation conditions.

Below, we show that, because of the high σ_{TPA} values of our photoinitiator, a nanosecond microlaser leads to the same polymerization speed as that obtained with femtosecond lasers and commercial UV resins. As kinetic parameters, k_p and k_t , are of the same order of magnitude for most usual monomers in radical chain polymerization,¹³ our comparison is based only on K_i and K_t . As an example of TPA fabrication using a commercial UV initiator and a femtosecond laser, we consider the experimental conditions employed by Kawata and co-workers.^{8,15}

For our photopolymerization experiments, the light source was a frequency-doubled Nd:YAG microlaser from Nanolase JDS Uniphase delivering 0.5-ns pulses with a 6.5-kHz repetition rate at the wavelength of 532 nm. An average power of 1.2 mW was used, and the laser was focused into a 1.8- μm -waist focal spot.¹¹ In our case, the factor K_i yields a value of $K_i = 6 \times 10^{58} \text{ photons}^2 \text{ m}^{-4} \text{ s}^{-2}$ at the center of the focal spot. The photopolymerization experiments by Kawata and co-workers were carried out with a mode-locked Ti:sapphire laser with a 150-fs pulse duration, a 76-MHz repetition rate, and 140-pJ pulse energy focused through a 1.4-N.A. objective lens. An approximate value of $K_t = 1 \times 10^{64} \text{ photons}^2 \text{ m}^{-4} \text{ s}^{-2}$ is obtained in these irradiation conditions. Therefore, by using a microlaser and weak focusing, we lose a factor of 10^5 on K_t .

Let us now compare the values of K_i . Our resin consisted of 3% photoinitiator [N^4, N^4' -bis-(4-methoxyphenyl)- N^4, N^4' -diphenyl-2,7-diamino-9,9-diethylfluorene], 70% monomer [tris(2-hydroxyethyl) isocyanurate triacrylate with a radical inhibitor level of 100 parts in 10^6] and 27% polymer binder [poly(styrene-co-acrylonitrile) (75/25)]. The synthesis, TPA cross section, electrochemical potential, and initiation properties of our photoinitiator were reported previously.¹¹ Its TPA cross section at 532 nm was found to be $\sigma_{\text{TPA}} = 8 \times 10^{-49} \text{ cm}^4 \text{ s photon}^{-1}$. The quantum yield Φ of the energy transfer between the excited photoinitiator and the monomer can be deduced from biomolecular quenching values already reported for molecules similar to our photoinitiator in presence of acrylates.¹⁶ Considering that the typical excited-state lifetime was 1 ns, we

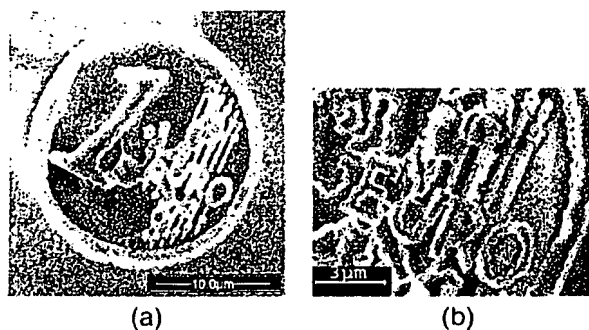


Fig. 2. Scanning electron microscope images of a 1-Euro coin, fabricated with a microlaser: (a) overview, (b) magnified detail.

found an approximate value of $\Phi = 10^{-3}$. In the case of commercial UV photoinitiators, they exhibit weak σ_{TPA} values. As an example, a value of $3.8 \times 10^{-56} \text{ cm}^4 \text{ s photon}^{-1}$ was measured by Miwa *et al.* on a commercial photoresin.¹⁷ This is 7 orders of magnitude lower than our photoinitiator's TPA cross section. However, the radical generation quantum yield of commercial photoinitiators is expected to be better than 10^{-1} . Therefore, the overall value of K_i is approximately 5 orders of magnitude higher for our resin than for commercial UV resins. This higher magnitude compensates for the lower value of K_i resulting from our irradiation source. Hence, the polymerization speed obtained is of the same order of magnitude in both experiments.

The threshold exposure for polymerization of our resin was determined to be 95 J/cm^2 ,¹¹ corresponding to a minimum exposure time of 4 ms to induce polymerization at the center of the beam. This time is of the same order of magnitude as the exposure times reported by Tanaka *et al.*¹⁵ In accordance with our predictions, polymerization speeds are comparable when one is using either our optimized photoinitiator and low-intensity exposure or a commercial UV initiator and tightly focused ultrashort laser pulses.

We created polymer microstructures with our microlaser to illustrate the large range of possibilities offered by the two-photon polymerization technique. Figure 2 displays scanning electron microscope images of a 1-Euro coin. The images were fabricated by point-by-point irradiation with a high-N.A. (1.3-N.A.) objective lens, allowing a focal spot of $\sim 0.2\text{-}\mu\text{m}$ radial size with an average power of $\sim 3 \text{ }\mu\text{W}$ to form. The distance between adjacent points was 200 nm. After the resin film was irradiated, we immersed it in acetone to dissolve the unexposed material, leaving only the polymer structure on the glass plate. The 1-Euro coin had a diameter of $20 \text{ }\mu\text{m}$, and features as small as 160 nm could be depicted on the micrograph. We believe that better spatial resolution can be attained through optimization of the irradiation conditions with respect to the resin photosensitivity. This aspect is under study.

In conclusion, we have shown that two-photon-initiated polymerization could be performed with a

common and inexpensive laser source, owing to the design of photoinitiators with large TPA. This result should encourage the widespread use of this versatile technique, which makes it possible to fabricate 3D microstructures of arbitrary complexity. We proposed a simple model to relate the progression of the polymerization process to the photopolymer and irradiation characteristics, providing a basis on which different experimental conditions can be compared. Using this model, we can clarify why our photoresin can be solidified by exposure to low intensities, at speeds equivalent to those obtained in other microfabrication experiments that employed femtosecond lasers.^{5,8,17}

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